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Studies on Camphor Series, XI.
Synthesis of Camphor, II.
Preparation of Liquid and Solid Camphenes from Pinene Hydrochloride by the Catalytic Dehydrochlorination of Copper Oxides.

By

Bunkichi Masumoto.

(Received June 28, 1926)

It was noticed by Prof. S. Komatsu, C. Fujio and T. Yukitomo,[1] that camphene, by the action of finely divided copper oxide on pinene hydrochloride, was obtained with a yield of nearly 90 %.

Repeating the same experiment, it was observed that the activity of the dehydrochlorination of copper oxides, though they are prepard equally from copper nitrate solution and ammonia water, varies with the conditions under which they are prepared, and therefore, in this experiment, the preparation of camphene from pinene hydrochloride by using the following eight varieties of copper oxides as catalyst was studied.

Copper oxides.

CuO (I) Copper hydroxide gel was prepared according to the method suggested by Bemmelen[2] from a cupric nitrate and a potassium hydroxide solution, which was washed with water three times, filtered, dried on a tone-plate, and ignited on a sand-bath heated to 250°–300°. The density of the oxide was 5.8135.

CuO (II) This was prepared from crystalline copper hydroxide

1 Unpublished paper.

2 Zs. anorg. Chem., **5**, 466(1894).

following Böttger's directions.[1] The greyish basic copper nitrate, prepared from cupric nitrate and 20% ammonia water, was boiled with a 6 % sodium hydroxide solution. The brown-coloured hydroxide thus formed, was centrifuged, washed with water five times, and ignited at 250°—300°. Its density was 4.9504.

CuO (III) A blue-coloured, amorphous copper hydroxide[2] which was obtained by diluting an ammoniacal copper nitrate solution with water, was filtered, washed and ignited at 250°—300°; its density was 4.2832.

CuO (IV) A basic copper nitrate of grey colour, which was obtained by the action of 20 % ammonia water on a boiling solution of copper nitrate, was ignited at 250°—300°. Its density was 5.4193.

CuO (V) A black cupric oxide was prepared from a copper nitrate solution and 20 % ammonia water, following the directions suggested by Mellor.[3] Its density was 5.2543.

CuO (VI) This was prepared in a similar manner to CuO (IV), but in this case an excess of ammonia water was employed. The density of the oxide was 5.3630.

CuO (VII) This was prepared from copper nitrate by ignition at 250°—300°. It coloured brownish black, and its density was 5.7683.

CuO (VIII) A hot aqueous solution of copper nitrate is treated with an excess of a sodium hydroxide solution, the precipitate thus formed, was washed, filtered and ignited at 250°. The density of the oxide was 6.3814.

Experiment.

Pinene hydrochloride which melts at 127° and shows $[\alpha]_D = +35.°67$ in an alcohol solution, was passed with a constant velocity over 8 gr. of the copper oxide mentioned above, heated at 220.°

As reaction proceeded, the colour of the catalyst changed from black or brown to yellow or yellowish grey, and water was noticed to form by the reaction, but no hydrogen chloride gas was evolved.

The reaction product was composed of oily and water layers which were weighed separately, and the latter was washed twice with a sodium carbonate solution, dried over anhydrous sodium carbonate, and then subjected to fractional distillation.

The physical and chemical properties of each fraction was studied, and the results are shown in the following tables. In the table, the fraction boiling at 150°—165° is assigned for camphene.

1 Zs. anorg. Chem., **5**, 474 (1894).
2 Bonsdorff: Ibid., **41**, 132 (1904).
3 Comprehensive treatise on inorg. chem., vol. III, p. 132.

Table I.

Catalyst.	d_4^{11}	Wt. increased of CuO.	H_2O formed.	Pinene-HCl used.	Velocity. gr./h.	Reaction product.	Yield of camphene.
CuO (I)	5·8135	3·5 gr.	1·5 gr.	20·6 gr.	27·4	16·0 gr.	63·4 %
CuO (II)	4·9504	3·5 〃	2·0 〃	20·9 〃	20·9	18·0 〃	74·6 〃
CuO (III)	4·2832	1·9 〃	1·5 〃	20·8 〃	28·0	17·5 〃	72·5 〃
CuO (IV)	5·4193	2·0 〃	1·1 〃	23·8 〃	31·7	20·0 〃	56·5 〃
CuO (V)	5·2543	1·6 〃	2·0 〃	21·1 〃	28·0	18·5 〃	62·5 〃
CuO (VI)	5·3630	2·4 〃	2·0 〃	20·4 〃	20·4	18·0 〃	71·5 〃
CuO (VII)	5·7683	0·3 〃	0·0 〃	20·3 〃	22·0	19·5 〃	14·4 〃
CuO (VIII)	6·3814	3·2 〃	2·1 〃	21·4 〃	21·4	18·0 〃	74·7 〃

Table II.

(a) CuO (I).

Fraction.	Yield.	n_D^{25}	d_4^{25}	Remarks. Cl.	Unsaturation
–150°	0·6 gr.	1·4610	/	–	+
150°–155°	5·1 〃	1·4625	0·86370	trace	+
155°–160°	3·9 〃	1·4645	0·86730	+	+
160°–165°	0·7 〃	1·4699	0·88095	+	+
165°–166°	0·4 〃	1·4746	/	+	trace
166°–	0·1 〃	/	/	+	–

(b) CuO (II).

Fraction.	Yield.	n_D^{25}	d_4^{25}	Remarks. Cl.	Unsaturation.
–140°	1·5 gr.	1·3475	/	+	–
140°–150°	0·3 〃	1·4605	/	+	+
150°–155°	2·1 〃	1·4615	0·86012	–	+
155°–160°	7·0 〃	1·4639	0·86248	–	+
160°–165°	2·9 〃	1·4673	0·86731	trace	+
165°–170°	0·9 〃	1·4721	/	+	+
170°–173°	0·5 〃	1·4775	/	+	+
173°–	0·9 〃	/	/	+	–

(c) CuO (III).

Fraction.	Yield.	n_D^{25}	d_D^{25}	Remarks. Cl.	Unsaturation.
140°–150°	0·9 gr.	1·4600	0·86348	+	+
150°–155°	3·6 〃	1·4629	0·86418	+	+
155°–160°	5·4 〃	1·4647	0·86488	+	+
160°–165°	2·0 〃	1·4726	0·88148	+	+
165°–	2·0 〃	/	/	+	−

(d) CuO (IV).

Fraction.	Yield.	n_D^{25} liq.	n_D^{25} solid.	M. Pt.	Remarks Cl.	Unsaturation.
150°–155°	2·8 gr.	/	1·4864	43°–44°	+	+
155°–160°	6·7 〃	/	1·4882	44°–45°	+	+
160°–165°	1·1 〃	1·4679	1·4880	47°–48°	+	+
165°–170°	1·4 〃	1·4710	1·4897	58°–59°	+	−
170°–190°	1·9 〃	1·4747	1·4891	/	+	−
190°–	2·3 〃	/	/	/	+	/

(e) CuO (V).

Fraction.	Yield.	n_D^{25} liq.	n_D^{25} solid	M. Pt.	Remarks. Cl.	Unsaturation.
130°–150°	0·5 gr.	/	1·4873	44°–45°	−	+
150°–155°	1·6 〃	/	1·4887	43°–44°	−	+
155°–160°	6·7 〃	/	1·4873	44°–45°	−	+
160°–165°	1·6 〃	1·4679	1·4896	46°–47°	+	+
165°–175°	0·3 〃	1·4713	1·4905	59°–61°	+	+
175°–190°	1·1 〃	1·4751	1·4899	89°–90°	+	−
190°	3·3 〃	/	/	/	+	/

(f) CuO (VI).

Fraction.	Yield.	n_D^{25} liq.	n_D^{25} solid.	M. Pt.	Remarks. Cl.	Remarks. Unsaturation
145°–150°	0·6 gr.	1·4626	1·4849	39°–40°	–	+
150°–155°	5·0 〃	1·4639	1.4863	42°–43°	–	+
155°–160°	5·0 〃	1·4655	1·4873	43°–44°	trace	+
160°–165°	0·9 〃	1·4627	/	/	+	+
165°–175°	0·3 〃	1·4727	/	/	+	+
175°–185°	0·5 〃	1·4769	/	/	+	+
185°–	0.5 〃	/	/	/	+	/

(g) CuO (VII).

Fraction.	Yield.	M. Pt	Remarks. Cl.	Remarks. Unsaturation.
130°–160°	1.3 gr.	52°–52°·5	+	+
160°-170°	1·0 〃	54°	+	+
170°-180°	1·0 〃	55°	+	–
180°–190°	1·5 〃	/	+	–
190°–195°	1·5 〃	/	+	–
195°–	8·5 〃	/	+	–

(h) CuO (VIII).

Fraction.	Yield.	n_D^{25}	d_4^{25}	Remarks. Cl.	Remarks. Unsaturation.
–130°	2·7 gr.	1·3483	/	+	–
130°–154°	1·3 〃	1·4602	0·85800	+	+
154°-160°	8·3 〃	1·4633	0·86054	trace	+
160°–165°	3·0 〃	1·4680	0·86582	+	+
165°–169°	1·4 〃	1·4737	0·90628	+	+
169°–	0·9 〃	/	/	+	/

As will be seen in the above tables, the catalytic activity of copper oxide on pinene hydrochloride, measured with the yield of camphene, is the same with CuO (II), (IV), (VI) and (VIII), and these catalysts could

be classified into two groups according to the physical state of the reaction product, camphene; one group denoted by A, to which CuO (I), (II), (VIII) and (III) belonged, by the catalytic actian of the oxides of this group a liquid camphene resulted from pinene hydrochloride. The other oxides were included into the other group, denoted by B, the action of these catalysts, solid camphene with a small quantity of liquid modification was usually obtained.

The copper oxides of the B group are, on the whole, prepared by ignition of copper nitrate or basic copper ni rate, while those of the A group are prepared from copper hydroxide, precipitated with a sodium hydroxide solution, hence a trace of some sodium compound such as sodium nitrate would be expected to remain as an impurity in the catalysts of the A group by adsorption, which might exert some influence, in the forming of liquid camphene, on the catalytic action of the copper oxide. The same experiment was repeated by using CuO (IV) as catalyst, to which 1 % sodium nitrate was added, but, contrary to my expectation, solid camphene was obtained with a yield of 63.4 % as will be seen in Table III.

Table III.

Fraction.	Yield.	Cl.	Unsaturation
150°–155°	2·1 gr.	–	+
155°–160°	6·4 〃	trace	+
160°–165°	1·8 〃	+	+
165°–175°	1·0 〃	+	+
175°–195°	2·0 〃	+	–
195°–	2·2 〃	+	/

When, however, dry hydrogen chloride gas alone passed for one hour over 5 gr. of copper oxides heated to 220°, it was noticed that in the case of the copper oxides of group A, the colour of the oxides changed from brown to yellowish grey, the weight of the catalyst increased, and water was formed; while no visible changes were produced in the case of those of B group, although both groups are capable of decomposing pinene hydrochloride into camphene under the same conditions. From these facts, it was anticipated some intimate relation might exist between the chemical reactivity of copper oxides with hydrogen chloride gas, and the physical states of camphene formed by the catalytic action

of the oxides on pinene hydrochloride.

Table IV.

Catalyst.		Weight increased.	Colour change.
A	CuO (I)	3·5 gr.	+
	CuO (II)	2·7 〃	+
	CuO (III)	1·6 〃	+
	CuO (VIII)	3·7 〃	+
B	CuO (V)	1·0 〃	−
	CuO (VI)	0·4 〃	−
	CuO (VII)	0·3 〃	−

It has been already mentioned by Komatsu and C. Fujio[1] that solid and liquid camphene could be obtained separately from pinene hydrochloride by using same catalyst such as ferric chloride at different temperatures.

As a matter of fact, as will be seen in the present research, any modification of camphene may result from pinene hydrochloride by choosing a suitable copper oxide as catalyst, though the interpreta ion for the formation of these two modifications, at present, is lacking.

The writer wishes to express his hearty thanks to Prof. S. Komatsu for his kind guidance and continual i terest in this work and also to the Association for the Commemoration of the Tercentenary Anniversary of the Tôsho Shrine for a research grant.

June, 1926. Laboratory of Organic and Bio-Chemistry.

1 Mem. Coll. Sci. Kyoto Imp. Univ., **7**, 389(1924).

The Arrangement of Micro-crystals in Beaten Gold Foil.

By

Shinsuke Tanaka.

(Received July 8, 1926)

ABSTRACT

The arrangement of the micro-crystals in rolled and beaten gold foil was investigated by the X-ray method. The majority of the micro-crystals in the rolled foils are so arranged that their (110) faces are parallel to the surface of rolling and the normals of the (211) faces parallel to the direction of rolling. In the case of a foil prepared by hammering for a long time, the (100) faces of the micro-crystals of the gold are arranged parallel to the surface of the foil the orientations in other respects being at random. In the intermediate stage of the hammering process, there seems to exist a comparatively persistent state, during which the micro-crystals take on roughly a fibrous structure with the normals of the (110) faces as their common axis lying nearly in the surface of the foil.

When the writer was carrying out his investigations on the arrangement of the micro-crystals in a rolled platinum foil, he found that in a gold leaf obtained from the market, the (100) faces of the micro-crystals were arranged parallel to the surface of the leaf, and he reported this fact in these memoirs.[1] A further investigation of this problem has lately been conducted and is described below.

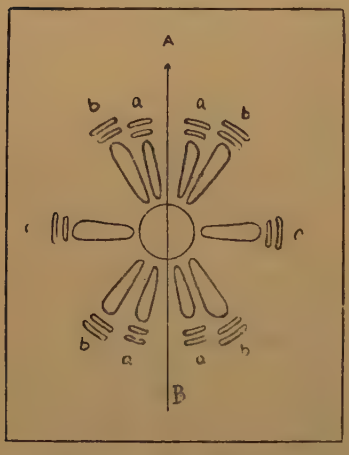
The gold leaves used in the present experiment were prepared by rolling and then hammering gold bullion: a piece of gold bullion was rolled down to a thin plate of the thickness of about 0·05mm., and then it was flattened to a very thin gold leaf by hammering. In order to prevent cracking and to keep the stretching uniform, the foils were held

(1) These Memoirs, **8**, 319 (1925).

between sheets of strong and smooth paper during the hammering process. In some cases the samples were annealed before hammering to destroy the regular arrangement of the micro-crystals caused by rolling, but this is not done in the making of gold leaf in the factory.

Using the K-radiation from the Mo. anticathode of a Coolidge tube, the writer examined the interference figures by the ordinary method of photographing the Laue spots, and the spectra of the X-rays reflected from the surface of the sample were examined by the aid of the same apparatus as was used in the previous experiment.[1]

Fig. 1′.



Two photographs corresponding to the rolled gold foils are reproduced in Fig. 1_A in Plate X and 1_B in plate XI. Fig. 1_A is a transmission photograph obtained under the normal in idence of the X-rays on the surface of the foil, and Fig. 1_B a reflection photograph. Fig. 1′ represents diagramatically Fig. 1_A in Plate X. AB in Fig. 1′ represents the direction parallel to that of rolling, and the radiating bands marked by a, b and c are caused by the reflection of the X-rays from the crystal faces denoted in the following Table I. The angles φ between the radiating bands and the line AB are given in the same table.

Table I.

Radiating bands	Indices of the faces	The angle φ
a	(111)	15°—17°
c	(111)	90°
b	(100)	33°—35°

If we disregard the weak band, this distribution of the radiating bands is entirely the same as that of the rolled platinum foil given in a former paper.[1] The spectral lines in Fig. 1_B in Plate XI show that the X-rays are reflected from the (110) faces arranged parallel to the surface of the rolled foil. This fact is also the same as in the case of a rolled platinum foil. As is generally known, the lattice of the crystals of gold and platinum belongs to the same form as the face-centered cubic. Therefore the identity of the distribution of the radiating bands in the transmission

1 These memoirs, **8**, 319 (1925). In the first column of Table 1. page 322 of that paper the third and the fourth horizontal row must be interchanged.

photograph and that of the reflecting surface which is responsible for the spectral lines in the reflection photograph indicates that the micro-crystals in a rolled gold foil are arranged in the same manner as in the rolled platinum foil, i. e. the majority of the micro-crystals in the gold foil take such an orientation that the (110) faces are nearly parallel to the surface of rolling and that the normals to the (211) faces are parallel to the direction of rolling.

If we beat the rolled foil to a thinner foil, then the photograph obtained by the transmission method, shows that the radiating band a in Fig. 1′ gradually approaches the band b, and that it coincides at last with the latter band as the process of beating is advanced. At this stage the radiating bands become six in all, and any neighbouring two of them make an angle of about 60°. At the same time the intensities of the parts of the bands corresponding to the continuous X-rays become weaker and the other parts of the bands corresponding to the K-radiation of the target become stronger. From the positions of these intense K lines of Mo., it was easily reconizable that the reflecting planes which produced these six bands were chiefly the (111) faces of the gold crystals. The appearance of these is shown in Figs. 2_A, 3_A and 4_A in plate X.

The photographs of the spectra of X-rays reflected from the surface of the foils, some of which are reproduced in Fig. 2_B, 3_B and 4_B in Plate XI, were taken at each stage of hammering. In these photographs four new spectral lines appear in addition to those observed in Fig. 1_B in Plate XI, and it was ascertained by calculation that they belong to the K_α and K_β lines of molybdenum reflected from the (311) and (100) faces of the gold crystals. Here it must be noted that the intensity of the lines corresponding to the (100) faces becomes gradually stronger as the process of hammering is advanced.

Next the sample was again beaten down to a very much thinner foil, the thickness being reduced to about 0·001 mm. or less. The photograph obtained by the transmission of X-rays through this thin foil consists of several very faint concentric rings characteristic of the disordered arrangement of the micro-crystals with respect to the direction of the X-ray beam. The photograph obtained by the reflection method consists of two spectral lines caused by the reflection of the X-rays from the (100) faces arranged parallel to the surface of the foil. Fig. 5_A in Plate X and Fig. 5_B in plate XI are reproductions of these photographs.

Fig. 2_C in Plate X is a reproduction of the photograph obtained from a sample which was annealed after rolling, and it indicates, by its irregular strips, that the regularity of the arrangement of the micro-crystals

is completely destroyed. With such annealed foils the writer could not observe any fine spectral lines in photographs obtained by the reflection-method. The annealed foils were hammered as in the case of unannealed foils, and at various stages of hammering the arrangement of the micro-crystals was examined by both the transmission and the reflection method. At the beginning the photographs obtained by the transmission method showed quite a different appearance from those obtained with una nealed foil as is seen in Fig. 3C, in Plate X; but as the process of hammering proceeded they began to resemble each other as shown in Fig. 4C, in Plate X. When the hammering is continued further and when the foils become very thin the transmission-photograph becomes entirely the same as the corresponding one obtained with unannealed thin foil.

The writer examined also the arrangement of the micro-crystals of the annealed and then hammered foil by the reflection-method. At the stage of hammering process corresponding to that between Fig. 3C and Fig. 4C in Plate X, the spectra caused by the reflection from the (311), (110) and (100) faces were recognized, these faces being arranged parallel to the surface of the foil. This fact is the same as that observed in the corresponding stage of unannealed foil. When the hammering was continued further with the annealed foil, only the spectrum caused by the reflection from the (100) faces was observed, as in the case of unannealed foil.

Here it must be noted that at no stage of the hammering could the writer find any spectral lines reflected from (111) faces on the photographs obtained by the reflection method though these faces are of the greatest atomic density, and the most efficient in reflecting the X-rays.

In the case of unannealed foil the micro-crystals in the foil whose (110) faces are arranged parallel to the surface of the sample at the beginning, seem to begin to change their positions by hammering, as stated before; and as the hammering process is still uther continued they take such orientations that their (100) faces lie parallel to the surface of the foil. It must be especially remembered that, during this process, the micro-crystals change their orientation in such a way that their (111) faces never come out parallel to the surface of the foil. We shall now consider the manner of this change of orientation of the micro-crystals.

First we shall consider the sample which gave the photographs reproduced in Figs. 4A and 4C in Plate X by the transmission metho l. This stage persists very long in the process of hammering whether the sample is annealed after rolling or not. These photographs were taken by the normal incidence of the X-rays on the surface of the foil, and

they consist of six radiating bands reflected from the (111) faces of the crystals, the angle between any neighbouring two of these bands being about 60°.

The presence of the radiating bands indicates that the micro-crystals in the sample have the arrangement generally known as the fibrous structure. When the micro-crystals in the foil have the same direction, defined crystallographically as common, and they are so distributed that each micro-crystal has a position produced by rotation at some angle around this common direction or "common axis," we call it a fibrous structure. Thus the determination of the direction of the fiber in the sample and the crystallographic direction of the common axis for each micro-crystal is the essential point in solving our problem. With regard to the direction of the fiber, we may determine it by taking many transmission photographs corresponding to various orientations of the sample against the incident X-ray beam. This is actually done by rotating the sample around several axes, and if we could find such an axis that no rotations around it makes any change in the photographs, this axis would be parallel to the direction of the fiber. If this axis of the fiber were known, the crystallographic direction of this axis would be determined from the distribution of the radiating bands.

Many photographs were taken in various orientations of the sample rotated about different axes parallel to the surface. But the result was not decisive, as the radiating bands were very diffuse. This is probably due to the fact that all the micro-crystals are arranged, not exactly in fibrous structure, but only roughly so, and many crystals may occupy different orientations deviating by some small angles from their mean fibrous axis. If we take into consideration the comparative irregularity of hammering as a method of working, this is of course natural. This is also in comformity with the actual observation that, at this stage of the hammering process, three different sets of spectra of X-rays are obtained by the reflection from three crystal faces, (311), (110) and (100) which are arranged nearly parallel to the surface of the foil.

It seems to be not unnatural to consider, from the experiments carried out by various authors, that some one of the normals of the prominent faces (111), (211), (110), or (100) of the micro-crystals are arranged roughly as the common axis of the fibrous structure. As stated before, the six radiating bands on the photograph are caused by the reflection of X-rays from the (111) faces. For the present, the direction of the common axis is taken provisionally to be in the surface of the foil, and by taking each normal above mentioned as the common axis,

Table 2

Common axis	Angles between two neighbouring bands	Total number of radiating bands
normal of (111)	71°, 38°	6
normal of (211)	43°, 38°, 28°	10
normal of (110)	70°, 55°	6
normal of (100)	110°, 70°	4

the positions of the radiating bands for one normal incidence of the X-rays to the surface of the foil were calculated and tabulated in Table 2. From this table the normal of the (110) faces seems to be suitably taken as the common axis.

Next the writer calculated the positions of the radiating bands when the normal of the (110) faces was taken as the common axis, and the X-rays were projected at various angles to this axis. The values are given in Table 3.

Table 3

Angle between the normals of the (110) faces and the X-rays	Angle between two neighbouring bands	Total number of radiating bands
20°	230°, 130°	2
30°	210°, 150°	2
40°	200°, 160°	2
50°	166°, 79°, 36°	4
60°	170°, 65°, 60°	4
70°	70°, 66°, 58°, 42°	6
80°	70°, 60°, 59°, 56°	6
90°	70°, 55°	6

From this table we know that when the angles between the X-ray and the common axis are not greatly different from 90°, the positions of the radiating bands are not subjected to any considerable change. If we take other normals as the common axis and calculate similarly the positions of the radiating bands, we have quite different values from those given in the above table, which can not possibly be accepted. Therefore it seems to be not unreasonable to take the normal of the (110) faces as the common axis which is arranged roughly parallel to the surface of the foil. With this as his starting point the writer could calculate the

positions of the radiating bands when the sample was rotated in various directions and found them to be in conformity with actual observation, though they are not given here.

In conclusion, the author wishes to express his sincere thanks to Prof. U. Yoshida under whose direction the work was done.

Fig. 2A.

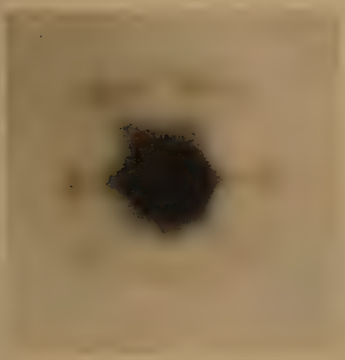


Fig. 2C.

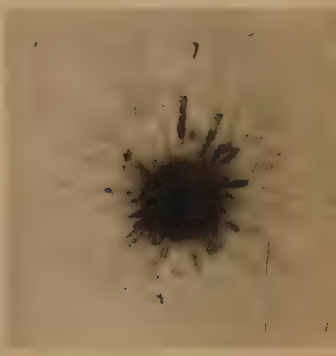


Fig. 1A.

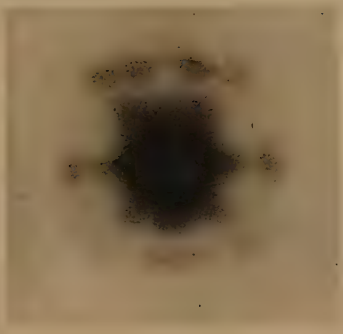


Fig. 3A.

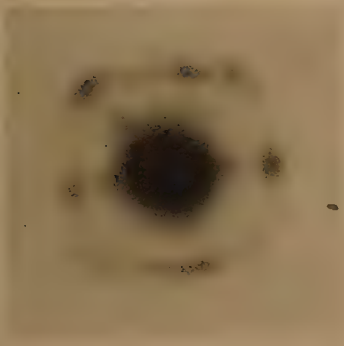


Fig. 3C.

Fig. 5A.

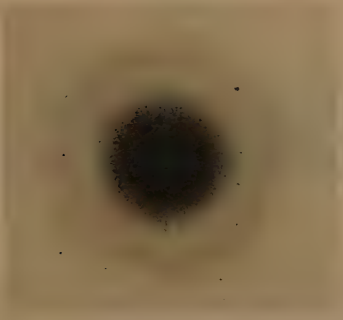


Fig. 4A.

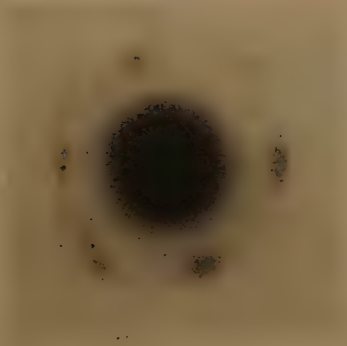
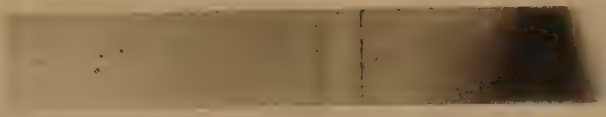


Fig. 4C.

(110)

Fig. 1B.



(311) (110) (100)

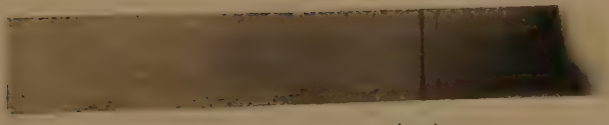
Fig. 2B.

(311) (110) (100)

Fig. 3B.

(311) (110) (100)

Fig. 4B.



(100)

Fig. 5B.

Condensation of Nitriles with Thiamides. III. Nitriles with Thioanilides and Thionaphthalides.

By

Seiichi Ishikawa.

(Received July 8, 1926)

Abstract.

The condensation of nitriles with thiamides in which the hydrogen atom of the imino-group is replaced by the aryl group was studied with the object of ascertaining whether iminosulphides are obtainable as the condensation-products or not, and if they are really produced, how they are related with imino-isothiamides described in the previous report. It was found that iminosulphides are generally very unstable yellow substances which, when exposed in moist air, quickly change their colour to red and then decompose. In the cases in which no iminosulphide could be isolated either its decomposition-product or another condensation-product deemed to have been produced from the decomposition-product was obtained.

In the First Report[1] on this piece of research, it was stated that benzonitrile and thiobenzamide condense with each other in such a manner that the imino-group of the latter combines with the cyanogen-group of the former, as shown below :

$$C_6H_5-\underset{\underset{SH}{|}}{C}=NH \;+\; \underset{\underset{N}{\|}}{C}-C_6H_5 \;=\; C_6H_5-\underset{\underset{SH}{|}}{C}=N-\underset{\underset{NH}{\|}}{C}-C_6H_5$$

Such condensation is therefore expected with certainty not to take place between nitriles and thioanilides or thionaphthalides, in which the hydrogen atom of the imino-group is replaced by phenyl or naphthyl.

To confirm this experimentally conde sation-experiments were conducted by passing dry hydrochloric acid gas into an ethereal solution of benzonitrile and thiobenzanilide, when no sign of condensation could be

1 S. Ishikawa, Mem. Coll. Sci., Kyoto Imp. Univ., **5**, 299 (1921).

observed, the solution retaining its original yellow colour even after standing over-night, and no condensation-product crystallizing out. But a yellow substance conceivable as a condensation-product was isolated when the mother-liquor was evaporated under diminished pressure. The action of heat or hydrochloric acid caused the change of its yellow colour to red and decomposed it into thiobenzamide and benzanilide in equimolecular proportion. (Experiment 1). The condensation-product thus obtained may be considered as imino-sulphide, since only one way of condensation is conceivable that in which the sulphydryl-group of thiobenzamide enters into combination with the cyanogen-group of benzonitrile, thus :

$$C_6H_5-\underset{\underset{N.C_6H_5}{\|}}{C}-SH + \underset{\underset{N}{\|\|}}{C.C_6H_5} = C_6H_5C(=N.C_6H_5)-S-\underset{\underset{N\,H}{\|}}{C}-C_6H_5$$

When phenylbenziminosulphide is hydrolysed by acids, its yellow colour always changes to red before decomposition, showing that something like an intermolecular change is taking place before its decomposition. The red intermediate compound being very unstable, its constitutional formula could not be experimentally determined, but inferring from the analogy that an atom-group of C−S−C=N or C−O−C=N rearranges to C−N−C=S or C−N−C=O[1], the mechanism of the decomposition of phenylbenzimino-sulphide may be explained as shown below :

$$C_6H_5C(=N.C_6H_5)-S-\underset{\underset{NH}{\|}}{C}\,C_6H_5 \rightarrow C_6H_5C(=N.C_6H_5)-N=\underset{\underset{SH}{|}}{C}\,C_6H_5 + H_2O$$

$$\rightarrow C_6H_5C(=N\,C_6H_5)-OH + HN = \underset{\underset{SH}{|}}{C}-C_6H_5$$

A condensation-product of acetonitrile and thiobenzanilide was also obtained as a yellow unstable substance which turns red by the action of acids and soon decomposes into benzanilide and thioacetamide. (Experiment 2).

The condensation-reaction between benzonitrile and α-thiobenznaphthalide or β-thiobenznaphthalide turned out a little different ; in neither case was iminosulphide isolated, thiobenzamide and benziminoisothiobenzomide

1 Hoffmann Ber. deut. chem. Ges., **19**, 2061 (1886); Billeter, Ibid., **26**, 1681 (1893); Knorr. **30**, 922 (1897); Wislicenus and Goldschmidt, Ibid., **33**, 1470 (1900); Wislicenus and Körber, Ibid., **35**, 164 (1902); Lander, Journ. Chem. Soc., **83**, 406 (1903); Wheeler and Johnson, Amer. Chem. Journ., **30**, 24 (1903); Wheeler, Johnson & McFarland, Journ. Amer. Chem. Soc., **25**, 787 (1903); Jamieson, Ibid., **26**, 177 (1904); Rivier and Schneider. Chem. Ztrbl. **1**, 643 (1920); Dixon and Taylor, Journ. Chem. Soc., **101**, 2512 (1912); **117**, 720 (1920); etc. Dixon and Kennedy, Ibid., **117**, 81 (1920).

being obtained in the former case and β-benznaphthalide in the latter. (Experiments 3 and 4). The results of these experiments, however, are not at all contradictory to those of the First and the Second Experiments. The production of thiobenzamide and benznaphthalide as well as that of benziminoisothiobenzamide may well be explained by assuming the primary formation of iminosulphide, as is clear from the following scheme:

$$C_6H_5C(=N\,C_{10}H_7)-SH \;+\; C(\equiv N)-C_6H_5 \;=\; C_6H_5C(=N\,C_{10}H_7)-S-C(=NH)\,C_6H_5$$

$$C_6H_5C(=N\,C_{10}H_7)-S-C(=NH)\,C_6H_5 \;+\; HCl \;=\; C_6H_5C(=N\,C_{10}H_7)-Cl \;+\; HS-C(=NH)-C_6H_5$$

$$C_6H_5-C(=NH)-SH \;+\; C(\equiv N)\,C_6H_5 \;=\; C_6H_5-C(-SH)=N-C(=NH)-C_6H_5$$

All other condensations between many different thioanilides or thionaphthalides and nitriles were found to take place in such a manner that the mechanism of the reaction could well be explained from the same point of view. It will probably be interesting to note that the reaction between thiobenznaphthalide and benzonitrile proceeds only to a small extent, while that between thiobenzanilide and benzonitrile takes place far better. A similar influence of a naphthyl radical on condensation was also observed in the case of thioacetonaphthalides.

The condensation of benzonitrile with thioacetanilide, α-thioacetonaphthalide and β-thioacetonaphthalide took place in an analogous way as in the cases of Experiments 3 and 4, giving thiobenzamide and benziminoisothiobenzamide as the reaction-products (Experiments 5, 6, 7). The amounts of thiobenzamide thus formed were calculated to correspond to 64, 10 and 10% of benzonitrile respectively. The condensation-reaction between acetonitrile and thioacetanilide was also examined, and thioacetamide was separated as the reaction-product, the amount of which corresponded to only 4% of the acetonitrile used. (Experiment 8).

Though acetonitrile thus condenses with thioacetanilide with great difficulty, it reacts with thioformanilide very smoothly giving nearly the theoretical yield of thioacetamide (Experiments 9 and 10). It may therefore be coucluded that the degree of condensation between nitriles and thioanilides is governed by the mutual relation of both the substances which partake in the condensation, but not by the property of either one of them.

Experimental part.

The thioanilides and thionaphthalides used in this investigation were prepared by the action of phosphorus pentasulphide upon anilides and naphthalides according to the method of Jacobson[1] and Wallach.[2]

1. Benzonitrile with Thiobenzanilide.

4·12 grams of benzonitrile and 8·53 grams of thiobenzanilide (molecular proportion) were dissolved together in absolute ether; and this solution, kept cool with a freezing-mixture, was saturated with dry hydrochloric acid gas, whereupon yellow crystals began to deposit gradually on the wall of the vessel, but no change of colour was observed in the solution even after a day. The crystalline substance was first deemed to be a condensation-product, but when it was taken out of the mother-liquor into the moist air, it immediately changed into a red mass which once again turned yellow quickly. The crystals separated from the mother-liquor were therefore washed with dry ether as quickly as possible and the last trace of hydrogen chloride and ether was removed in a vacuum, great care being taken to avoid moisture. They melted at 98° without decomposition and were proved to be nothing but thiobenzanilide. The colour change in the moist air was found, by the next experiment, to be due to a condensation-product adhering to thiobenzanilide.

The mother-liquor was evaporated under reduced pressure, great care being taken to avoid any trace of moisture by attaching an apparatus containing phosphorus pentoxide to the evaporating vessel. When a small portion of the yellow residue obtained on evaporation was taken out of a vacuum desiccater into the moist air, it turned red immediately and finally changed into a yellow mass as was observed above. The yellow substance was found to contain no trace of thiobenzanilide and was separated into thiobenzamide and benzanilide by treating it with ether. The amounts of thiobenzamide and benzanilide separated from a portion of the yellow mass were 0·5374 gram and 0·7280 gram respectively, corresponding to 1 mol of the former and 0·94 mol of the latter. From this result it is clear that the residue which was obtained by the evaporation of the mother-liquor is really a condensation-product. It melted at about 60° to a red liquid and was easily hydrolysed by hydrochloric acid, first changing its colour to red. Without further purifying, it was analysed with the following results:

1 Jacobson, Ber., **19**, 171 (1886); **20**, 1897 (1887); **21**, 2627 (1888).
2 Wallach, Ibid., **16**, 145 (1883).

1. 0·2408 gram of the sample gave 0·1844 gram of $BaSO_4$
2. 0·2826 gram of the sample gave 0·1973 gram of $BaSO_4$

	Found		Cal. $C_{20}H_{16}N_2S$
	(1)	(2)	
S	10·51	9·58	10·14

The molecular weight of the substance was determined by the cryoscopic method, its benzene solution being used.

Benzene 19·5696 grams, the substance 0·1227 gram, depression of the freezing point 0·095°.

	Found	Cal. $C_{20}H_{16}N_2S$
Mol. weight	323	316

2. Acetonitrile with Thiobenzanilide.

1·64 grams of acetonitrile and 8·53 grams of thiobenzanilide (molecular proportion) were dissolved in 200 c.c. of ether, and into this solution dry hydrochloric acid gas was conducted, when the solution acquired a reddish tint which soon became yellow, a considerable amount of yellow crystals being deposited. No colour change was observed in the solution even after standing 12 hours. When the crystals separated out from the mother-liquor were taken out in the moist air, they became instantly red and gradually decomposed leaving a yellow substance. This decomposition-product dissolved completely in ether, leaving no trace of the benzanilide which was anticipated to be present in it. It was washed with water, and about 6·0 grams of thiobenzanilide melting at 98° were obtained. A small amount of thioacetamide was also detected in the aqueous washings from which it was extracted with ether. The residue obtained by the evaporation of the mother-liquor was a yellow resinous substance which became red at once in the moist air and gradually decomposed into a yellow mass. The decomposition-product was washed with water and then with a dilute caustic soda solution to remove thioacetamide and thiobenzanilide, and the white mass obtained thus was crystallized from a mixture of benzene and petroleum ether. The crystals melted at 159° and were found to be benzanilide from the result of the following analysis:

0·3145 gram of the sample produced 19·1 c.c. of nitrogen gas at 29·3° and 772·3 mm.

	Found	Calc. $C_{13}H_{11}NO$
N	6·97	7·11

The amount of benzanilide was about 0·6 gram, and this corresponds to about 8% of the thiobenzanilide used. From the aqueous washings a

small quantity of thioacetamide and from the caustic soda solution about 1·5 grams of thiobenzanilide were isolated. The total amount of recovered thiobenzanilide was 7·5 grams (about 96% of the thiobenzanilide used). An attempt to isolate a condensation-product was not successful, owing to the poorness of the yield and its instability. From the quantities of thiobenzanilide and benzanilide obtained above, it is roughly calculated that about 9% of the acetonitrile had reacted upon the thiobenzanilide.

3. Benzonitrile with α-Thiobenznaphthalide.

2·06 grams of benzonitrile and 5·26 grams of α-thiobenznaphthalide (molecular proportion) were dissolved together in 150 c.c. of ether, and the solution was treated with hydrochloric acid gas, whereupon the colour of the solution changed to red, and a large amount of yellow crystals separated out. The crystals were α-thiobenznaphthalide hydrochloride, mixed with a small quantity of a condensation-product. The latter crystallized in red needles from a mixture of benzene and petroleum ether. It melted at 70° and produced dibenzenylazosulphime when oxidized with iodine. From these properties and others it is clear that this substance is benziminoisothiobenzamide. On evaporating the mother-liquor a minute quantity of thiobenzamide was isolated.

4. Benzonitrile with β-Thiobenznaphthalide.

150 c.c. of ether in which 2·06 grams of benzonitrile and 5·26 grams of β-thiobenznaphthalide (molecular proportion) were dissolved, was saturated with hydrogen chloride in the usual way, whereupon the colour of the solution was gradually converted red. On standing over-night, a large amount of β-thiobenznaphthalide hydrochrolide mixed with some condensation-products separated out. The latter consists of red needles, melting at 72° and was easily oxidized to dibenzenylazosulphime with an alcoholic iodine solution. It is therefore evident that this substance is benziminoisothiobenzamide. The same substance was also found in a residue obtained by evaporating the mother-liquor. About 0·3 gram of white needle crystals melting at 155° was also isolated from the residue. They were analysed with the following result and confirmed to be β-benznaphthalide.

0·2533 gram of the sample gave 12·1 c.c. of nitrogen gas at 17·8° and 766·5 mm.

	Fonnd	Calc. $C_{17}H_{13}NO$
N	5·66	5·67

Beside these, about 0·2 gram of thiobenzamide was also isolated.

5. Benzonitrile with Thioacetanilide.

3·09 grams of benzonitrile and 4·54 grams of thioacetanilide (molecular proportion) were dissolved in 150 c.c. of ether, and this solution was treated with hydrogen chloride in the usual way, whereupon a yellow crystalline substance immediately began to deposit and frequently stopped up the delivery tube, making the passage of the gas impossible. The solution remained nearly unchanged till the solution saturated with hydrochloric acid gas was left to stand over-night when it became vividly coloured red. From the yellow crystals separated from the mother-liquor thioacetanilide was isolated.

A residue obtained by evaporation of the mother-liquor was treated with an aqueous solution of sodium bicarbonate and extracted with ether. The ethereal extract thus obtained was evaporated, and the residue, after having been washed with warm water to remove the admixed substances, was recrystallized from a mixture of benzene and petroleum ether. About 0·2 gram benziminoisothiobenzamide was obtained. Besides this about 2·5 grams of thiobenzamide and some acetanilide were also found in the residue left on evaporation of the mother-liquor.

In the above experiments about 22% of thioacetanilide was recovered unchanged and about 64% of benzonitrile was converted into thiobenzamide, showing that about 71% of each of the substances taken had entered into condensation.

6. Benzonitrile and α-Thioacetonaphthalide.

2·06 grams of benzonitrile and 4·02 grams of α-thioacetonaphthalide (molecular proportion) were dissolved in 150 c.c. of ether, and the solution was treated with hydrochloric acid gas. The colour of the solution changed gradually to red. After standing over-night, the mother-liquor was poured out and evaporated under reduced pressure, and the residue was neutralized with an aqueous solution of sodium bicarbonate and washed with hot water until the washings became colourless. A mixture of white needles with a red substance was obtained, from which 0·25 gram of α-acetonaphthalide, 0·06 gram of benziminoisothiobenzamide and 0·27 gram of thiobenzamide were separated.

From the yields of thiobenzamide and benziminoisothiobenzamide it was calculated that about 11% of the benzonitrile had thus been converted into thiobenzamide.

7. Benzonitrile with β-Thioacetonaphthalide.

An ethereal solution containing 3·09 grams of benzonitrile and 6·3 grams

of β-thioacetonaphthalide (molecular poprortion) was treated with hydrochloric acid gas, and a result analogous to that of Experiment 6 was obtained. The amount of benzonitrile converted into thiobenzamide was a little less, being 9%.

8. Acetonitrile and Thioacetanilide.

In the condensation-experiment conducted in a similar manner by passing hydrogen chloride into an ethereal solution of acetonitrile and thioacetanilide, no special product was obtained, except a small quantity of thioacetamide which was confirmed by analysing its platinum double salt according to the method of Ray:[1]

0·1308 gram of the double salt gave 0·0560 gram of platinum on ignition.

	Found	Calc. $(CH_3 . CSNH)_3PtCl_2HCl$
Pt	42·81	43·20

9. Benzonitrile with Thioformanilide.

4·12 grams of benzonitrile and 5·48 grams of thioformanilide (molecular proportion) were dissolved in 120 c.c. of ether, and the solution was saturated with hydro hloric acid gas. The solution became red in a few minutes, but no crystals were observed to deposit even after 12 hours. From the crude crystalline residue obtained by evaporating the red solution in a vacuum a small qnantity of benziminoisothiobenzamide, aniline and about 5·0 grams of thiobenzamide were separated. The percentage of benzonitrile which was converted into thiobenzamide was about 91%.

10. Acetonitrile and Thioformanilide.

1·23 grams of acetonitrile and 4·11 grams of thioformanilide (molecular proportion) were dissolved in 120 c.c. of ether, and the solution was saturated with hydrochloric acid gas. The solution became orange-yellow, but no precipitate separated out even after 12 hours. The residue obtained by the evaporation of the solution under reduced pressure was found to contain aniline hydrochloride (4·5 gram) and thioacetamide

The author wishes to express his sincere thanks to Prof. M. Matsui for the interest he has taken throughout this investigation and also to Prof. O. Kubota of The Seventh Higher School for his valuable advice.

1 Ray, Journ. Chem. Soc., **115**, 871 (1919).

Organic Compounds of Arsenic. V. The Electrolytic Reduction of 3-nitro-4-hydroxyphenylarsinic acid.

By

Kaoru Matsumiya and **Hisakazu Nakata.**

(Received August 16, 1926)

Abstract.

The electrolytic reduction of 3-nitro-4-hydroxyphenylarsinic acid in an acid solution was studied with the object of obtaining the chemically pure organic compounds of arsenic related to salvarsan. The influence of the electrode material. current density, temperature, concentration of acid, etc., was investigated, and it was found that the cathode material and the concentration of acid have remarkable effects. Mercury, lead amalgam cathodes gave similar results which differ altogether from those given by the other cathodes. When mercury, lead, or lead amalgam was taken as the cathode, and a hydrochloric acid solution as the cathode solution, the strength of the hydrochloric acid showed such a noteworthy effect that so far as its strength was kept weaker than 4. 7 normal, the reduction product was 3-amino-4-hydroxyphenylarsine while 3,3-diamino-4,4-dihydroxyarsenobenzene dihydrochloride was precipitated when the acidity became stronger. Sulphuric acid, however, showed no such influence of its strength, 3-amino-4-hydroxyphenylarsine having been always produced as its final product.

In the course of the studies on the synthesi of the organic compounds of arsenic for therape tic purposes, it was found necessary to prepare the reduced compounds of 3-nitro-4-hydroxyphenylarsinic acid in chemically pure state. As one of the methods which were expected to meet such a demand electrolytic reduction was chosen.

As to the electrolytic reduction of 3-nitro-4-hydroxyphenylarsinic acid there are two patents, one in Germany and the other in America. The former[1] gives no precise description concerning the resulting products;

1. H. Bart, D. R. P., 270568.

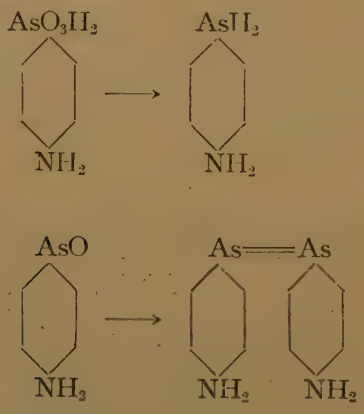
and the latter[1] avers the obtaining of 3-amino-4-hydroxyphenylarsinic acid in an alkaline solution.

As arsenic acid radical[2] is not reduceable in an alkaline medium, our experiments were conducted in an acidic medium. The following are the results obtained by reducing 3-nitro-4-hydroxyphenylarsinic acid with a mercury cathode in a hydrochloric acid solution.

The nitro group and the arsinic acid radical of 3-nitro-4-hydroxyphenylarsinic acid were both reduced energetically and 3-amino-4-hydroxyphenylarsine was produced. It was now found that the strength of the hydrochloric acid in the cathode solution has a remarkable influence upon the reduction, that is, when rather weak hydrochloric acid was used, 3-amino-4-hydroxyphenylarsine was the product, which remained dissolved in the cathode solution, while 3,3–diamino–4,4–dihydroxyarsenobenzene dihydrochloride (salvarsan) was produced as a yellow-coloured powder, when the strength of the hydrochloric acid was more than 4 7 normal.

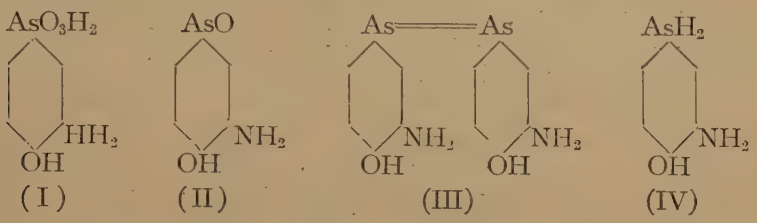
3-amino-4-hydroxyphenylarsine thus electrochemically obtained was found to be purer than that ever obtained by chemical methods. So far as we know, there is no statement in chemical literature that salvarsan has ever been prepared electrolytically from 3-nitro-4-hydroxyphenylarsinic acid.

A cording to Fichter and Elkind's study[3] of the electrolytic reduction of organic compounds of arsenic, 4–aminophenylarsinic acid is reduced to 4–aminophenylarsine, while more easily reduceable 4–aminophenylarsine oxide gives p-arsenoaniline which belongs to a less reduced stage than the corresponding arsine; thus,



1. A. Mouneyrat, U. S. P., 1232373.
2. F. Fichter and E. Elkind, Ber., **49**, 240 (1916)
3. loc. cit.

Now the successive reduction stages of 3-amino -4-hydroxyphenylarsinic acid traced by ordinary chemical reaction are as follows:



(I) (II) (III) (IV)

In our electrolytic experiments compounds (III) and (IV) were obtained from 3-nitro-4-hydroxyphenylarsinic acid. Consequently we regarded at first the electrolytic reduction of 3-nitro-4-hydroxyphenylarsinic acid to have taken place similarly, passing from (I) to (IV) succesively and 3, 3-diamino-4,4-dihydroxyarsenobenzene to be an intermediate reduction product. The fact that 3,3-diamino-4,4-dihydroxyarsenobenzene dihydrochloride is separated as precipitates in a hydrochloric acid solution more concentrated than 4·7 normal was also deemed to be due to its difficult solubility in concentrated hydrochloric acid.

By closer study, however, many contradictory facts were found out. First, when hydrochloric acid was added to 0·25 % solution of 3,3-diamino-4, 4-dihydroxyarsenobenzene dihydrochloride the precipitation of the dihydrochloride took place as soon as the strength of the hydrochloric acid in the solution just reached 2·5 normal. In our electrolytic experiment the precipitation of the dihydrochloride was observd to occur only when the concentration of hydrochloric acid was more than 4·7 normal, (the concentration of 3-nitro-4-hydroxyphenylarsinic acid at that moment was 1,6%). Secondly, when dilute sulphuric acid was used instead of hydrochloric acid, no precipitation was recognized during the electrolysis, and no reduction product other than 3-amino-4-hydroxyphenylarsine was found in the solution. If 3,3-diamino-4,4-dihydroxyarsenobenzene were produced in the course of reduction, it must have been instantly precipitated as the sulphate, for it is practically insoluble in water. Thirdly, when 3-nitro-4-hydroxyphenylarsinic acid, dissolved in a 2·5 normal solution of hydrochloric acid, was reduced by passing exactly the theoretical quantity of electricity neccesary to reduce it to diamino dihydroxyarsenobenzene, and the resulting product was precipitated by neutralising the cathode solution with sodium bicarbonate, nothing but 3-amino-4-hydroxyphenylarsine could be isolated.

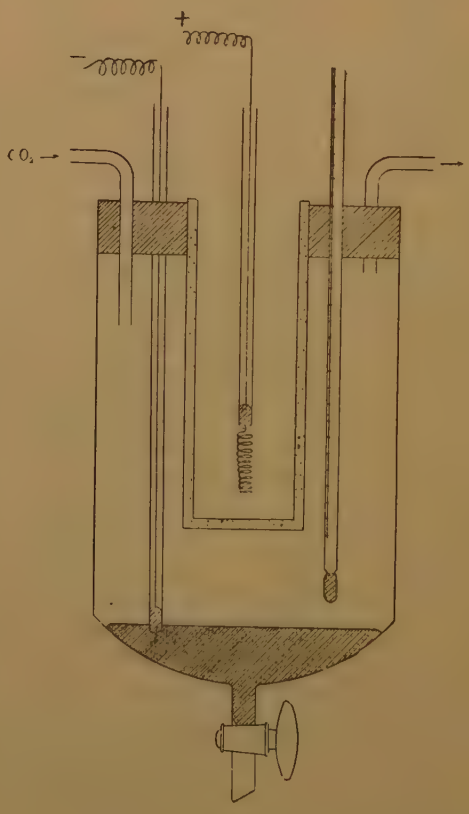
These facts indicate that 3,3-diamino-4,4-dihydroxyarsenobenzene can not be regarded necessarily as the intermediate product which precedes the

formation of 3-amino-4-hydroxyphenylarsine by the electrolytic reduction of 3-nitro-4-hydroxyphenylarsinic acid. The oxidation of 3-amino-4-hydroxyphenylarsine in the cathode solution to the corresponding arseno-compound by atmospheric oxygen is hardly imaginable, as the cathode chamber was entirely filled with carbon dioxide.

EXPERIMENTAL PART

Preliminary Experiment.

As almost all the reduction products of 3-nitro-4-hydroxyphenylarsinic acid hitherto known are easily oxidizable, the electrolytic reduction of the acid was performed in the atmosphere of carbon dioxide. This was effected by the aid of the apparatus sketched below. A porous cell containing hydrochloric acid and a platinum anode was used as the anode compartment, and it was tightly inserted into a cathode cell by means of a cork provided with a glass tube holding a platinum wire connected with the cathode, and a thermometer and two delivery tubes for the passage of the carbon dioxide. The cathode cell consisted of a glass vessel containing mercury which served as the cathode. As the catholyte a hydrochloric acid solution of 3-nitro-4-hydroxyphenylarsinic acid was taken.



1. The cathode solution was prepared by suspending 5 grms. of 3-nitro-4-hydroxyphenylarsinic acid in a mixture of 100 c. c. of water and 30 c. c. of hydrochloric acid (1.19), and as the anode solution a 20 % solution of hydrochloric acid was taken; the

surface area of the mercury cathode was 12·5 sq. cm.. Keeping the temperature at 30°–35° a current of 2·6 amperes was passed. During the electrolysis some arsine gas was always observed to evolve from the cathode though the contrary is stated in the German patent[1]. At the end of the electrolysis, that is, after about two hours from the beginning, the cathode solution became clear and colourless. When it was kept in the atmosphere of carbon dioxide over night, fine needle crystals (I) separated out. These were separated and dried in vacuo over sulphuric acid. On neutralizing the filtrate with sodium bicarbonate white precipitates (II) were obtained which were also collected and dried.

The crystals (I) were observed to decompose at about 180° and were soluble in water, alcohol and dilute mineral acid, but insoluble in ether and concentrated hydrochloric acid. Their aqueous solution reacted acidic to litmus, and on neutralizing the solution with an alkali, white precipitates were formed which redissolved in an excess of the precipitant. It became black on standing in the air. From these properties and the following analytical results the substance was recognized to be 3-amino-4-hydroxyphenylarsine hydrochloride. Arsenic was estimated by Ewins' method.[2]

0·1182grm. subst. required 9·85 c. c. N/10 iodine solution.
0·1227grm. subst. gave 0·0513grm. H_2O and 0·1360grm CO_2.
0·2449grm. subst. required 11·19 c. c. N/10 H_2SO_4.
0·1431grm. subst. gave 0·0855 grm. AgCl.

	Found	Calc. for $C_6H_9ONAsCl, H_2O$
As	31·25	31·29
C	30·23	30·07
H	4·68	4·63
N	6·40	5·85
Cl	14·78	14·80

To verify that the arsenic was in the form $-AsH_2$, the substance was titrated with an iodine solution which oxidizes the former into the corresponding arsinic acid. During the titration a sodium bicarbonate solution was constantly dropped to keep the solution slightly acidic. The amount of the iodine required was found exactly to coincide with that of the theoretical: 0·1619 grm. subst. required 40·96 c.c. N/10 iodine solution. (Calc. 40·56 c.c.)

1. loc. cit.
2. A. J. Ewins, J. Chem. Soc., **109**, 1355 (1916).

The precipitates (11) decompose at 140°–150° and were soluble in alcohol, ether, dilute mineral acid and alkali, but sparingly so in water When a dilute hydrochloric acid solution of the substance was dropped into concentrated hydrochloric acid fine needle crystals identical with crystals (1) separated. Thus the substance was confirmed to be free 3-amino-4-hydroxyphenylarsine. The result of the estimation of arsenic was as follows:—

0·1330 grm. subst. required 14·30 c.c. N/10 iodine solution.

	Found	Calc. for C_6H_8ONAs.
As	40·32	40·51

The total yield of 3-amino-4-hydroxyphenylarsine was found to be 80 %.

2. The cathode solution was prepared by dissolving 2 grms. of 3-nitro-4-hydroxyphenylarsinic acid in a mixture of 60 c.c. of water and 60 c.c. of hydrochloric acid (1·19), and 6 N. hydrochloric acid was used as the anode solution. Keeping the temperature at 20°–25°, a current of 2 amperes was passed, and then yellow precipitates were gradually deposited. After about one hour and a half, when the precipitates ceased to increase, the current was cut off, and the yellow precipitates were collected on a filter and dried in vacuo over sulphuric acid.

The yellow substance was seen to be soluble in water, methyl alcohol and dilute hydrochloric acid, insoluble in ether and conc. hydrochloric acid. Its aqueous solution reacted acidic to litmus. On neutralizing its solution with alkali, yellow precipitates were produced which redissolved in an excess of the precipitant. From the aqueous solution yellowish-white precipitates were formed by the addition of dilute sulphuric acid. This yellowish substance was easily oxidizable, and on exposing it in the air its colour slowly turned red and then black. It had no distinct melting point and decomposed at 180°–190°. These properties indicate that the substance is 3,3–diamino–4,4–dihydroxyarsenobenzene dihydrochloride, and this was comfirmed by the following results of the analysis:

0·1749grm. subst. gave 0·1053grm. AgCl.

0·1294grm. subst. required 10·95 c.c. N/10 iodine solution.

	Found	Calc. for $C_{12}H_{14}O_2N_2As_2Cl_2.2H_2O$
Cl	14·89	14·93
As	31·73	31·56

The yield was about 25 %.

The mother liquor having a yellow colour was diluted, and one part of it was titrated with an iodine solution in the presence of sodium bicarbonate, and the arsenic content was determined by Newbery's method[1]. The quantity of N/10 iodine solution required for the whole solution was found to be 197·5 c.c. and the amount of arsenic was estimated to be 0·3725 grm. The quantity of N/10 iodine solution required for 0·3725 grm. arsenic is calculated to be 198·7 c.c. if the arsenic be in the form –As=As–, but 298·14 c.c. if it be in the form $-AsH_2$. Thus it is clear that the 3-nitro-4-hydroxyphenylarsinic acid used was entirely reduced to 3,3-diamino-4,4-dihydroxyarsenobenzene.

3. Two grms. of 3-nitro-4-hydroxyphenylarsinic acid were dissolved in 125 c.c. of 2·5 N. sulphuric acid, and treated in the same way as in experiment 1, dilute sulphuric acid having been taken as the anode solution. On passing a current of 2 amperes for one hour and a half, the yellow-coloured cathode solution became quite colourless. It was neutralized with sodium bicarbonate, and 3-amino-4-hydroxyphenylarsine was obtained as white precipitates, the yield being 58 %.

Quantitative Investigation.

1. *Influence of the Quantity of Electricity.*

Cathode: mercury. (12·56 sq. cm.)
Anode: platinum.
Cathode solution: 2grms. of 3-nitro-4-hydroxyphenylarsinic acid.
100 c.c. of water.
25 c.c. of hydrochloric acid (1·19).
Anode solution: dilute hydrochloric acid.
Current: 2·6 amperes.

Time (hour)	Current quantity (amp-hour)	3-amino-4-hydroxyphenylarsine produced (grm)	Material yield (%)
1	2·6	1·26	89·6
1 1/6	3·0	1·29	91·4
1 1/3	3·5	1·33	94·8
2	5·2	1·32	93·9*

* 3-amino-4-hydroxyphenylarsine seems to to decompose owing to a prolonged electrolysis.

1. G. Newbery, J. Chem. Soc., **127**, 1751 (1925).

Temperature: 30°,

Treatment after electrolysis——The cathode solution was diluted with water to 500 c.c., and 20 c.c. of it was titrated with N/10 iodine solution in the presence of sodium bicarbonate.

2. *Influence of temperature.*

Current: 2·5 amperes.

Time: 1 1/5 hours.

The other conditions were the same as in the previous case. Treatment after electrolysis——The cathode solution was neutralized with sodium bicarbonate, and the precipitates of 3-amino-4-hydroxyphenylarsine were collected and weighed.

Temperature	3-amino-4-hydroxyphenylarsine obtained (grm)	Material yield (%)	Current efficiency (%)
2-7°	0·88	62	51·0
25°	0·96	68	54·4
50°	0·90	64	52·2

Thus the most favorable temperature was found to be 25°.

3. *Influence of current density.*

Temperature: 25°

Current: 2 amperes.

Time: 1 1/3 hours.

The other conditions were the same as in the foregoing case.

Area of cathode. (sq. cm.)	Cur. density (amp/sq. cm)	3-amino-4-hydroxy-phenylarsine (grm)	Material yield (%)	Cur. eff. (%)
7·16	0·28	1·08	76·0	76·5
12·56	0·16	1·02	72·5	73·0
25·00	0·08	0·95	67·5	67·9

4. *Influence of the concentration of mineral acid.*

Cathode solution: { 2 grms. of 3-nitro-4-hydroxyphenylarsinic acid. / 125 c.c. of hydrochloric or sulphuric acid

Anode solution: { hydrochloric or sulphuric acid of the same concentration as the cathode solution.

Time: 1 1/2 hours.

The other conditions were the same as in the preceding case.

Normality of hydrochloric acid	3-amino-4-hydroxy phenylarsine (grm)	3,3-diamino-4, 4-dihydroxyareseno-* benzene dihydrochloride (grm)
2·4	0·94	0
4·2	0·92	0
4·7	0·90	0
5·1	.....	0·22
6·2	.....	0·40

Normality of sulphuric acid	3-amino-4-hydroxy-phenylarsine (grm)	3,3-diamino-4, 4-dihydroxyarseno-benzene dihydrochloride (grm)
2·5	0·81	0
5·0	0·55	0
8·0	0·20	0

The number for 3-amino-4-hydroxyphenylarsine shows the quantity precipitated by neutralization with sodium bicarbonate, and that for 3,3-diamino-4,4-dihydroxyarsenobenzene dihydrochloride shows the amount actually precipitated during the electrolysis.

To confirm what substance would result when weak hydrochloric acid was used, and the calcurated quantity of electrocity for 3,3-diamino-4,4-dihydroxyarsenobenzene was passed, the following experiment was carried out.

Two grms. of 3-nitro-4-hydroxyphenylarsinic acid dissolved in a 2·5 normal solution of hydrochloric acid were reduced by passing a 2 ampere current for one hour (2·0 ampere-hours). The resulting solution was treated with sodium bicarbonate, and 0·36 grm. of a substance was obtained whose properties coincided with those of 3-amino-4-hydroxyphenylarsine. The content of arsenic estimated by Ewins' method was 36·91 %, the theoretical amount being 40·51. To confirm whether the arsenic was in the form $-AsH_2$, or $-As=As-$, it was directly titrated with an N/10 iodine solution, and 0·1138 grm. of the substance required 32·70 c.c., the theoretical amounts of iodine required for the form $-AsH_2$ and the form $-As=As-$ being 33·62 c.c, and 22·30 c.c. respectively. Thus it was known to be impure 3-amino-4-hydroxyphenylarsine.

* Described in experiment 7.

5. *Influence of the cathode material.*

The influence of the cathode material is remarkable. When mercury. lead, or lead amalgam was used as the cathode, 3-amino-4-hydroxyphenylarsine was obtained, while other materials, such as copper, nickel, platinum gave entirely different results. The results of reduction with mercury, lead, and lead amalgam were as follows :-

Cathode : mercury, lead, or lead amalgam. 25 sq. cm.
Anode : platinum spiral.
Cathode solution : { 2 grms. of 3-nitro-4-hydroxyphenylarsinic acid. / 100 c.c. of water. / 25 c.c. of hydrochloric acid (1·19).
Anode solution : 2·5 normal solution of hydrochloric acid.
Current : 2·5 amperes.
Time : 1 1/5 hours.
Temperature : 23°-25°

After electrolysis the cathode solution was titrated with an N/10 iodine solution.

Cathode material	3-amino-4-hydroxyphenylarsine (grm)	Material yield (%)	Current efficiency (%)
lead	0·73	51·9	42·3
lead amalgam	1·08	76·7	61·7
mercury	1·24	88·1	72·0

6. *Influence of solvent*

The influence of the solvent used for the cathode solution was not noticeable.

Cathode : mercury.
Anode : platinum.
Cathode solution : { 2 grms. of 3-nitro-4-hydroxyphenylarsinic acid dissolved in the solvent described below.
Anode solution : { hydrochloric acid of the same strength as that in the cathode solution.
Current : 2 amperes.
Temperature : 25°.
Time : 1 1/2 hours.

Solvent used for cathode solution	Normality of acid	3-amino-4-hydroxy-phenylarsine (grm)	3,3-diamino-4,4-dihydroxyarsenobenzene dihydrochloride(grm)
60 c.c. of ethyl alcohol 25 c.c. of HCl(sp. gr. 1·19) 35 c.c. of water	2·6	0.70[1]	0
60 c.c. of ethyl alcohol 40 c.c. of HCl (sp. gr. 1·19) 20 c.c. of water	4·2	0.48[1]	0
60 c.c. of ethyl alcohol 50 c.c. of HCl (sp. gr. 1·19) 10 c.c. of water	5·1	0.48[2]	
60 c.c. of ethyl alcohol 60 c.c. of HCl (sp. gr. 1·19)	6·2	.....	0.75[3]
60 c.c. of methyl alcohol 60 c.c. of HCl (sp. gr. 1·19)	6·2	.....	0.55[3]

7. *Study of a prolonged electrolysis*

As stated before (Exp. 4), the concentration of hydrochloric acid used in the cathode solution has an important bearing upon the reduction, 3,3-diamino-4,4-dihydroxyarsenobenzene dihydrochloride being the main reduction-product when hydrochloric acid is stronger than 4·7 normal, and 3-amino-4-hydroxyphenylarsine, when it is weaker.

As, however, it was considered beyond doubt that arsenobenzene would be more or less reduced to the corresponding arsine compound by a prolonged electrolysis, the following two experiments were carried out using 2·4 N-hydrochloric acid in the one, and 6·2 N-acid in the other.

Cathode: mercury.
Anode: platinum.
Cathode solution: 2 grms. of 3-nitro-4-hydroxyphenylarsinic acid.
120 c.c. of hydrochloric acid
Anode solution: hydrochloric acid.
Current: 2 amperes.
Temperature: 25°

1. Quantities obtained by neutralising the cathode solution with sodium bicarbonate.
2. The same as above. Titration with iodine solution showed it to be a mixture of 3-amino-4-hydroxyphenylarsine and 3,3-diamino-44,-dihydroxyarsenobenzene in the ratio of 7 : 3.
3. Quantities precipitated in the course of electrolysis.

During the electrolysis, a portion of the cathode solution was taken out at some interval and titrated with an N/10 iodine solution.

Time.	The quantity of iodine required for the whole cathode solution.	
	(2·4 normal solution)	(6·2 normal solution)
1 ¼ h	332·0 c.c.	287·5 c.c.
1 ½ h	392·0 c.c.	315·0 c.c.
2 h	397·5 c.c.	365·0 c.c.

The theoretical amounts of the N/10 iodine solution required are calulated as follows:

When reduced to the arsine stage	When reduced to the arseno stage
461·5 c.c.	307·7 c.c.

It is therefore, clearly to be seen that in the 6·2 normal acid solution 3-nitro-4-hydroxyphenylarsinic acid is completely reduced to 3,3-diamino-4,4-dihydroxyarsenobenzene after electrolysis for 1½ hours, and when the electrolysis is further prolonged the reduction goes on still further to produce 3-amino-4-hydroxyphenylarsine.

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